

Project D: Methods for Addressing the Hazards of Time Sensitive Chemicals



Presented by Helena Whyte



Time Sensitive Materials

- All materials that will develop additional hazards upon prolonged storage.



Misconception

- Time sensitive materials are not the same as shock sensitive chemicals where all hazards associated with the material are known when the material is purchased and do not change with time such as:
 - Shock sensitive
 - Pyrophoric, etc.



Core Members

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- Dan Marsick, DOE liaison
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Ad Hoc Members

- Rich Kelley, LLNL
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- John Piatt, PNL
- Jim Withers, Ames
- Jonathan Tapia, LANL



Project D Goal

- White paper describing best practices for managing time sensitive materials.



HISTORY

- Definitions 1/24/03
- What MSDSs miss 2/12/03
- Peroxide test data ongoing
- References, occurrences 4/19/03
- White paper outline 4/19/03
- Manuscript 1 6/11/03
- Manuscript 2 7/16/03
- Manuscript 3 outline 10/22/03



Four Categories of Time Sensitive Chemicals

- Peroxide formers
- Peroxide initiation of polymerization
- Evaporation of a stabilizer
- Form hazardous by-products over time, or decompose with overpressurization



Peroxide Former

- All materials that can react over time with air to form hazardous levels of peroxides.
- Identification
 - structure
 - reference materials
 - MSDS (sometimes)



Peroxide Former/Hazardous Polymerization

- All materials that will react over time with air to form peroxides that are capable of catalyzing or initiating a hazardous polymerization reaction.
- Identification same as for peroxide formers.



Materials that Dehydrate

- Materials that can become sensitive to localized thermal or mechanical shock at normal temperatures and pressures due to the evaporation of a solvent or stabilizer.
- Includes picric acid and collodion.



Materials That Generate Additional Hazards

- Materials that can react with air or other substances over time to generate significant, additional hazards.



Surprises

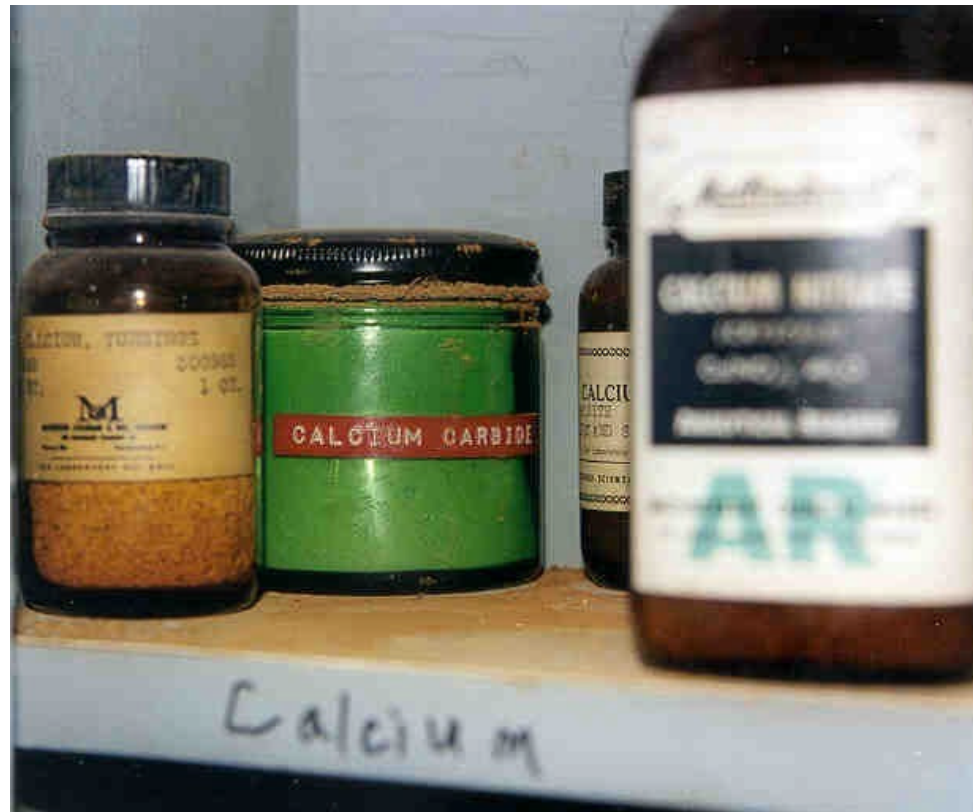
- Cyclohexane
- Peroxide measurement inaccuracies (poly peroxide effect)
- High boiling/viscous solvents thought not to form peroxides
- Costs
 - 20 liters of Compublend neutralized to 120 liters



Manuscript 1

- Management of Time Sensitive Chemicals Part 1: Misconceptions Leading to Incidents

Bulging Lid



Anhydrous HF





Black Potassium





Manuscript 2

- Management of Time Sensitive Chemicals Part II: Their Identification, Chemistry, and Management



Take Home Lesson

- The Table handout indicates why a list is useless
- Track chemicals by structure
- Time sensitive chemical owners need to be technically capable

Chemical Name	CAS#	# Samples	PPM Peroxide	Age (years)	Test Method & Comments (a)	Reference
Acetal	105-57-7	2	10 to 30	6 to >10	(f)	{l}
Acetaldehyde	75-07-0	6	1 to 20	>1 (g) to 8	(f)	{34} {m}
Acetophenone	98-86-2	2	2 to 3	>1 (g)		{34}
Acrylonitrile	107-13-1	2	0	>1 (g)		{m}
Amyl Acetate	628-63-7	1	0	>9	(f)	{l}
Benzaldehyde	100-52-7	1	1	(g)	(f) (b)	{l}
Benzyl Alcohol	100-51-6	9	0 to 100	>1 (g) to 11		{34} {m}
1-butanol	71-36-3	4	0 to 4	>1 (g)		{34} {l}
2-butanol	78-92-2	11	3 to >1,000	>1 (g)	(f)	{34} {3} {l} {m}
2-butoxyethanol	111-73-2	1	>100	>1 (g)	(f)	{l}
2-butoxyethylacetate	112-06-2	1	3	>1 (g)	(f)	{l}
Chloromethyl methyl ether	107-30-2	1	1	>10	(f)	{l}
Collodion	Mixture	2	0 to <10	>9 to >21	(f) (b)	{l}
"Compublend"	Mixture	2	30	>12	(f)	{l}
Crown Ether and Toluene	Mixture	1	1	> 8	(f)	{l}
Cumene	98-82-8	2	3 to 30	>9	(f)	{l}
Cyclohexane	110-82-7	2	<10 to >100	<9 to >9	(e) (f)	{l}
Cyclohexanol	108-93-0	8	3 to 2,000	>1 (g) to 30		{3} {34} {l} {m}
Cyclohexanone	108-94-1	9	1 to 3	>1 (g)		{34}
Cyclohexene	110-83-8	5	0 to 50	>1 (g) to 30	(f)	{34} {m}
2-cyclohexen-1-ol	822-67-3	1	30	>1 (g)		{34}
Cyclohexene oxide	286-20-4	1	1	>1 (g)		{34}
Cyclopentanol	96-41-3	1	3	>1 (g)		{34}
Cyclopentanone	120-92-3	4	1 to 4	>1 (g)		{34}
Dicyclopentadiene	77-73-6	1	3	>1 (g)	(f)	{l}
5-decyne	1942-46-7	1	10	>1 (g)	(f)	{l}
Dibenzyl ether	103-50-4	1	1	>1 (g)		{34}
2,5-dimethyltetrahydrofuran	1003-38-9	1	10	>1 (g)	(f)	{l}
Dimethoxymethane	109-87-5	2	>100	<2 to >10	(f)	{l}
3,4-dimethoxybenzyl alcohol	93-03-8	1	3	7	(f)	{l}
2,2-dimethoxypropane	77-76-9	2	3 to 10	>1 (g)	(f)	{l}
1,4-dioxane	123-91-1	18	0 to >100	>1 (g) to 24	(f)	{34} {l} {m}
1,4-dioxane, Laser Dye	Mixture	9	3 to 30	>9	(f) (b)	{l}
Dipropylene glycol methyl ether	34590-94-8	1	3	30	(f)	{l}
Dipropyl ketone	123-19-3	1	1	>10	(f)	{l}
Ethylbenzene	100-41-4	2	6 to 8	>1 (g)		{34}
Ethyl Ether	60-29-7	52	0 to >100	>1 (g) to 12.5	(f) (c)	{34} {l} {m}
Ethylene glycol dimethyl ether	110-71-4	9	0 to 100	0.5 to >1 (g) to 9	(f)	{l} {m}
Ethylene glycol monobutyl ether	111-76-2	7	1 to 3	>1 (g) to >9	(f) (b)	{l}
Ethyl methyl ketone	78-93-3	1	1	>1 (g)	(f)	{l}
Ethyl acetoacetate	141-97-9	1	30	>10	(f)	{l}
4-heptanol	589-55-9	1	30	>1 (g)		{34}
3-heptanone	541-85-5	1	2	>1 (g)		{34}
2-hexanol	626-93-7	1	10	>1 (g)		{34}
Isoamyl alcohol	123-51-3	48	0 to >1,000	0.5 to >1 (g) to 30	(f) (c)	{l} {m}
Isobutyraldehyde	78-84-2	1	2	>1 (g)	(f)	{34}
Isopentyl alcohol	123-92-2	2	100	>1 (g)	(f)	{l}
Isopropyl alcohol	67-63-0	32	0 to >100	>1 (g) to >9	(f) (b)	{l}
BIS(2-methoxyethyl) ether	111-96-6	2	1	>1 (g) to >10	(f)	{l}
Methyl acetate	79-20-9	2	0	>9	(f) (b)	{l}
3-methyl-1-butanol	123-51-3	7	10 to 30	>1 (g)		{34}
1-methylcyclohexene	591-49-1	1	1	>1 (g)		{34}
3-methylcyclohexene	591-48-0	1	3	>1 (g)		{34}
4-methylcyclohexene	591-47-9	1	1	>1 (g)		{34}
Methyl ethyl ketone	78-93-3	9	1 to >100	>1 (g) to >10	(f)	{l}
Methyl isobutyl ketone	108-10-1	10	0 to 70	1 to >1 (g) to >9	(f) (b) (i)	{34} {l} {m}

Chemical Name	CAS#	# Samples	PPM Peroxide	Age {years}	Test Method & Comments (a)	Reference
3-methyl-3-hexanol	597-96-6	1	>20	>1 (g)		{3}
4-methyl-2-pentanol	108-11-2	1	20 to 30	>1 (g)		{3} {34}
Methyl methacrylate	80-62-6	1	<10	>9	(f) (b)	{l}
2-methyltetrahydrofuran	96-47-9	5	0 to 100	>1 (g) to >10	(f)	{l}
Nitrocellulose	9004-70-0	2	0	>9	(f)	{l}
1-octanol	111-87-5	1	20	>1 (g)		{3}
2-octanol	123-96-6	2	2 to 20	>1 (g)		{3} {34}
1-octene	111-66-0	3	3 to 10	>1 (g)		{34}
2,4-pentanedione	123-54-6	1	1	>1 (g)	(f)	{l}
2-pentanol	6032-29-7	3	1 to 20	>1 (g)		{3} {34}
2-pentanone	107-87-9	5	1 to 12	>1 (g) to >10	(f)	{34} {l}
3-pentanone	96-22-0	2	4 to 6	>1 (g)		{34}
4-penten-1-ol	821-09-0	1	20	>1 (g)		{34}
1-pentene	109-67-1	5	1 to 10	>1 (g) to >10	(f) (d)	{34} {l}
Phenethyl alcohol	60-12-8	1	100	>1 (g)	(f)	{l}
1-phenylethanol	1514-69-7	3	30	1		{34} {m}
2-phenylethanol	60-12-8	2	10, 12	1 to >1 (g)		{34}
DL-1-phenylethanol	1517-69-7	1	>20	>1 (g)		{3}
Petroleum ether	109-66-0	9	<10 to >100	>9	(f) (b)	{l}
1-propanol	71-23-8	3	1 to >100	>1 (g) to 27	(f) (b)	{3}
2-propanol	67-63-0	28	0 to 100	>1 (g) to >10	(f) (b)	{34} {l}
Propiophenone	93-58-3	1	3	>1 (g)		{34}
Styrene	100-42-5	4	3	>1 (g) to >9	(f) (j)	{l}
Tetrahydrofuran	109-99-9	86	0 to >1,000	1 to 15	(f) (b) (k)	{34} {l} {m}
Tetrahydrofuran + water	Mixture	1	>100	>1 (g)	50:50 mix	{l}
M-bond Adhesive, Tetrahydrofuran	Mixture	50	<100	>9	(f)	{l}
1,2,3,4-tetrahydronaphalene	119-64-2	4	0	>9	(f)	{1} {m}
Vinyl acetate	108-05-4	1	0	3		{m}

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a) Test strips were obtained from Aldrich Chemical Co.

Tests were performed under an inert atmosphere following the manufacturer's instructions.

b) Some samples stored in an amber glass bottle.

c) One container was unopened.

d) Sealed in a glass ampoule.

e) Visible clusters of crystals present.

f) Tested with Dip Strip

g) Most likely greater than 1 year but ultimate age unknown.

h) Visible crystals in one container.

i) The 1 year old sample contained 70 ppm peroxide.

j) One partially polymerized, one fully polymerized.

k) One was HPLC grade, one with septum.

l) Data provided by David Blair

m) Data provided by Lawrence Berkeley National Lab



Required Elements of Chemical Management Program

- Identification
- Tracking system
- Storage conditions
- Inspection period and methodology



Required Elements (Cont.)

- Define “unsafe” condition
- Procedures for treating, transporting, and calling for assistance
- Acquisition of time sensitive chemicals
- Management support!



Manuscript 3

- Management of Time Sensitive Chemicals Part III: Stabilization and Treatment



In Preparation

- Treatment of “unsafe” time sensitive materials should only be conducted by trained, experienced technicians.
- Treatment must follow RCRA rules.
- Treatment requires proper PPE.



Future Efforts

- Reactive chemistry manuscript?
- Appendix to Chemical Management Handbook: Reactive and Shock Sensitive Chemicals?